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⑩ ② **CANADIAN PATENT**

⑤④ **DETERGENT COMPOSITIONS**

⑦⑩ Storm, Thomas D. and Nirschl, Joseph P., Cincinnati,
Ohio, U.S.A.

Granted to The Procter & Gamble Company, Cincinnati,
Ohio, U.S.A.

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Background of the Invention

The instant invention relates to granular built laundry detergent compositions which provide simultaneous laundering and softening of textiles during conventional fabric laundering operations. Such compositions employ a combination of non-scap synthetic detergent compounds, organic or inorganic detergent builders and particular smectite clay compounds having particular cation exchange characteristics.

10 Various clays materials have been utilized in many different types of detergent systems for widely diverse purposes. Clays, for example, have been disclosed for utilization as builders (Schwartz and Perry, Surface Active Agents, Interscience Publishers, Inc., 1949, pp. 232 and 299); as water-softeners (British Patent 461,221); as anti-caking agents (U.S. Patents 2,625,513 and 2,770,600); as suspending agents (U.S. Patents 2,594,257, 2,594,258 and 2,920,045); and as fillers (U.S. Patent 2,708,185).

20 It is also well known that some clay materials can be deposited on fabrics to impart softening and antistatic properties thereto. Such clay deposition is generally realized by contacting fabrics to be so treated with aqueous clay suspensions (See, for example, U.S. Patents 3,033,699 and 3,594,221).

Attempts, however, to incorporate clay materials into built detergent systems for the purpose of providing simultaneous fabric laundering and softening have not been entirely successful. Conventional detergent builders tend to retard or inhibit the tendency of clay materials to deposit on fabric surfaces, such deposition being necessary to
30 realize the desired fabric softening results. Furthermore, to provide the requisite uniform deposition of clay material



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onto fabrics being laundered. the clay material must be thoroughly and quickly dispersed throughout the fabric laundering solution during the relatively brief wash cycle.

Some of these difficulties of providing through-the-wash clay softening have been resolved by utilizing conventional fabric softening agents such as isostearic acid or

polyamine or polyquaternary ammonium compounds in combination with clay in built detergent formulations (See U.S. Patents 3,594,212 and 3,625,935). The dispersability problem can be

10 alleviated somewhat by adding to laundering solutions built liquid detergent compositions wherein clay is suspended and therefore more easily dispersed (See U.S. Patent 2,920,345).

However, such liquid heavy-duty built laundry compositions do not provide the convenience associated with granular laundry products.

Accordingly, it is an object of the present invention to provide compositions which can be employed to yield simultaneous fabric laundering and fabric softening.

20 It is a further object of the present invention to provide such laundering and softening compositions in the form of built granular formulations.

It has surprisingly been discovered that by utilizing particular types of clay having particular cation exchange characteristics, these objectives can be realized and built granular fabric laundering and softening compositions can be obtained which are unexpectedly superior to similar compositions known to the prior art.

Summary of the Invention

30 The present invention encompasses granular built laundry detergent compositions comprising: (a) from about 2% to about 30% by weight of a non-soap synthetic detergent

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selected from the group consisting of anionic synthetic detergents, ampholytic synthetic detergents, zwitterionic synthetic detergents and mixtures thereof; (b) from about 10% to about 60% by weight of an organic or inorganic detergent builder salt; and (c) from about 1% to about 50% by weight of a smectite-type clay softening agent having an ion exchange capacity of at least about 50 meq/100 g. such compositions provide a solution pH of from about 7 to about 12 when dissolved in water at a concentration of about 0.12% by weight. In a method aspect, the invention encompasses methods for concurrently cleansing and softening fabrics comprising laundering said fabrics in an aqueous laundry bath containing an effective amount (e.g., from about 0.02% to about 2% by weight) of a laundry detergent composition as described above.

Detailed Description of the Invention

Compositions of the instant invention comprise three essential components -- synthetic non-soap detergent, builder salt and clay. Each component is described in detail as follows:

Synthetic Detergent

From about 2% to about 30% by weight, preferably from about 5% to about 20% by weight, of the instant compositions comprise a non-soap synthetic detergent selected from the group consisting of anionic synthetic detergents, ampholytic synthetic detergents, and zwitterionic synthetic detergents. Examples of synthetic detergents of these types are described as follows:

Anionic Detergents

Anionic synthetic detergents include water-soluble salts, particularly the alkali metal salts, of organic sulfuric

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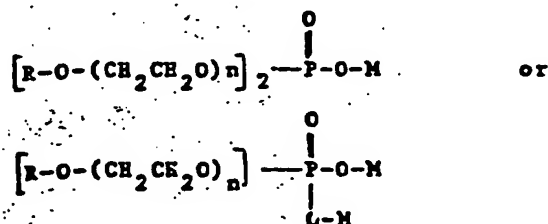
reaction products having in their molecular structure an alkyl group containing from about 8 to about 22 carbon atoms and a moiety selected from the group consisting of sulfonic acid and sulfuric acid ester moieties. (Included in the term alkyl is the alkyl portion of higher acyl moieties.) Examples of this group of synthetic detergents which form a part of the preferred built detergent compositions of the present invention are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols ($C_8 - C_{18}$ carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium and potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 20 carbon atoms in straight chain or branched-chain configuration, e.g. those of the type described in United States Patents Numbers 2,220,099 and 2,477,383 (especially valuable are linear straight chain alkyl benzene sulfonates in which the average of the alkyl groups is about 11.8 carbon atoms and commonly abbreviated as $C_{11.8}$ LAS); sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium and potassium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol (e.g. tallow or coconut oil alcohols) and about 1 to 6 moles of ethylene oxide; sodium and potassium salts of alkyl phenol ethylene oxide ether sulfates with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl groups contain from about 8 to about 12 carbon atoms.

Anionic phosphate surfactants are also useful in the present invention. These are surface active materials having substantial detergent capability in which the anionic

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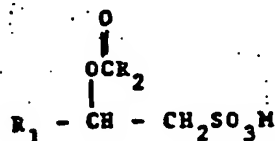
solubilizing group connecting hydrophobic moieties is an oxy acid of phosphorus. The more common solubilizing groups, of course, are $-SO_3H$ and $-SO_3Na$. Alkyl phosphate esters such as $(R-O)_2PO_3H$ and $ROPO_3H_2$ in which R represents an alkyl chain containing from about 8 to about 20 carbon atoms are useful herein.

These phosphate esters can be modified by including in the molecule from one to about 40 alkylene oxide units, e.g., ethylene oxide units. Formulae for these modified phosphate anionic detergents are



in which R represents an alkyl group containing from about 8 to 20 carbon atoms, or an alkylphenyl group in which the alkyl group contains from about 8 to 20 carbon atoms, and M represents a soluble cation such as hydrogen, sodium, potassium, ammonium or substituted ammonium; and in which n is an integer from 1 to about 40.

Another class of suitable anionic organic detergents particularly useful in this invention includes salts of 2-acyloxy-alkane-1-sulfonic acids. These salts have the formula



where R_1 is alkyl of about 9 to about 23 carbon atoms (forming with the two carbon atoms an alkane group); R_2 is alkyl of 1 to about 8 carbon atoms; and M is a water-soluble cation.

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The water-soluble cation, M, in the hereinbefore described structural formula can be, for example, an alkali metal cation (e.g., sodium, potassium, lithium), ammonium or substituted-ammonium cation. Specific examples of substituted ammonium cations include methyl-, dimethyl-, and trimethyl- ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperidinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like.

Specific examples of beta-acyloxy-alkane-1-sulfonates, or alternatively 2-acyloxy-alkane-1-sulfonates, useful herein include the sodium salt of 2-acetoxy-tridecane-1-sulfonic acid; the potassium salt of 2-propionyloxy-tetradecane-1-sulfonic acid; the lithium salt of 2-butanoyloxy-tetradecane-1-sulfonic acid; the sodium salt of 2-pentanoyloxy-pentadecane-1-sulfonic acid; the sodium salt of 2-acetoxy-hexadecane-1-sulfonic acid; the potassium salt of 2-octanoyloxy-tetradecane-1-sulfonic acid; the sodium salt of 2-acetoxy-heptadecane-1-sulfonic acid; the lithium salt of 2-acetoxy-octadecane-1-sulfonic acid; the potassium salt of 2-acetoxy-nonadecane-1-sulfonic acid; the sodium salt of 2-acetoxy-uncosane-1-sulfonic acid; the sodium salt of 2-propionyloxy-docosane-1-sulfonic acid; the isomers thereof.

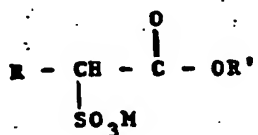
Preferred beta-acyloxy-alkane-1-sulfonate salts herein are the alkali metal salts of beta-acetoxy-alkane-1-sulfonic acids corresponding to the above formula wherein R_1 is an alkyl of about 12 to about 16 carbon atoms, these salts being preferred from the standpoints of their excellent cleaning properties and ready availability.

Typical examples of the above described beta-acetoxy

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alkanesulfonates are described in the literature: Belgium Patent 650,323 issued July 9, 1963, discloses the preparation of certain 2-acyloxy alkanesulfonic acids. Similarly, U.S. Patents 2,094,451 issued September 28, 1937, to Guenther et al. and 2,086,215 issued July 6, 1937 to DeGroote disclose certain salts of beta-acetoxy alkanesulfonic acids.

Another preferred class of anionic detergent compounds herein, both by virtue of superior cleaning properties and low sensitivity to water hardness (Ca++ and Mg++ ions) are the alkylated α -sulfocarboxylates, containing about 10 to about 23 carbon atoms, and having the formula



wherein R is C₈ to C₂₀ alkyl, M is a water-soluble cation as hereinbefore disclosed, preferably sodium ion, and R' is short-chain alkyl, e.g., methyl, ethyl, propyl, and butyl. These compounds are prepared by the esterification of α -sulfonated carboxylic acids, which are commercially available, using standard techniques. Specific examples of the alkylated α -sulfocarboxylates preferred for use herein include:

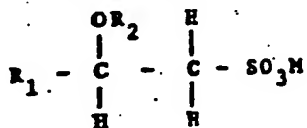
ammonium methyl- α -sulfopalmitate,
triethanolammonium ethyl- α -sulfostearate,
sodium methyl- α -sulfopalmitate,
sodium ethyl- α -sulfopalmitate,
sodium butyl- α -sulfostearate,
potassium methyl- α -sulfolaurate,
lithium methyl- α -sulfolaurate,

as well as mixtures thereof.

A preferred class of anionic organic detergents

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are the β -alkyloxy alkane sulfonates. These compounds have the following formula:



where R_1 is a straight chain alkyl group having from 6 to 20 carbon atoms, R_2 is a lower alkyl group having from 1 (referred) to 3 carbon atoms, and M is a water-soluble cation as hereinbefore described.

10 Specific examples of β -alkyloxy alkane sulfonates, or alternatively 2-alkyloxy-alkane-1-sulfonates, having low hardness (calcium ion) sensitivity useful herein to provide superior cleaning levels under household washing conditions include:

potassium-8-methoxydecanesulfonate,
sodium 2-methoxytridecane-sulfonate,
potassium 2-ethoxytetradecylsulfonate,
sodium 2-isopropoxyhexadecylsulfonate,
lithium 2-t-butoxytetradecylsulfonate,
20 sodium β -methoxyoctadecylsulfonate, and
ammonium β -n-propoxydodecylsulfonate.

Other synthetic anionic detergents useful herein are alkyl ether sulfates. These materials have the formula

$\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$ wherein R is alkyl or alkenyl of about 10 to about 20 carbon atoms, x is 1 to 30, and M is a water-soluble cation as defined hereinbefore. The alkyl ether

sulfates useful in the present invention are condensation products of ethylene oxide and monohydric alcohols having

about 10 to about 20 carbon atoms. Preferably, R has 14

30 to 18 carbon atoms. The alcohols can be derived from fats,

e.g., coconut oil or tallow, or can be synthetic. Lauryl

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alcohol and straight chain alcohols derived from tallow are preferred herein. Such alcohols are reacted with 1 to 30, and especially 6, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 5 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Specific examples of alkyl ether sulfates of the present invention are sodium coconut alkyl ethylene glycol ether sulfate; lithium tallow alkyl triethylene glycol ether sulfate; and sodium tallow alkyl hexaoxyethylene sulfate.

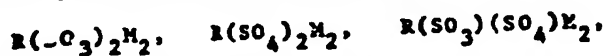
Preferred herein for reasons of excellent cleaning properties and ready availability are the alkali metal coconut- and tallow-alkyl oxyethylene ether sulfates having an average of about 1 to about 10 oxyethylene moieties. The alkyl ether sulfates of the present invention are known compounds and are described in U.S. Patent 3,332,876, to Walker (July 25, 1967).

Additional examples of anionic non-soap synthetic detergents, which come within the terms of the present invention are the reaction product of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other anionic synthetic detergents of this variety are set forth in United States Patents 2,486,921; 2,486,922; and 2,396,278.

Additional examples of anionic, non-soap, synthetic detergents, which come within the terms of the present invention, are the compounds which contain two anionic

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functional groups. These are referred to as di-anionic detergents. Suitable di-anionic detergents are the disulfonates, disulfates, or mixtures thereof which may be represented by the following formulae:



where R is an acyclic aliphatic hydrocarbyl group having 15 to 20 carbon atoms and M is a water-solubilizing cation, for example, the C₁₅ to C₂₀ disodium 1,2-alkyldisulfates, C₁₅ to C₂₀ dipotassium-1,2-alkyldisulfonates or disulfates, 10 disodium 1,9-hexadecyl disulfates, C₁₅ to C₂₀ disodium-1,2-alkyldisulfonates, disodium 1,9-stearyldisulfates and 6,10-octadecyldisulfates.

The aliphatic portion of the disulfates or disulfonates is generally substantially linear, thereby imparting desirable biodegradable properties to the detergent compound.

The water-solubilizing cations include the customary cations known in the detergent art, i.e., the alkali metals, and the ammonium cations, as well as other metals in group IIA, IIB, IIIA, IVA and IVB of the Periodic Table 20 except for boron. The preferred water-solubilizing cations are sodium or potassium. These dianionic detergents are more fully described in British Letters Patent 1,151,392 which claims priority on an application made in the United States of America (No. 564,556) on July 12, 1966.

Still other anionic synthetic detergents include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfo-succinamate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecyl-30 sulfo-succinamate; diethyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl

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esters of sodium sulfosuccinic acid.

Other suitable anionic detergents utilizable herein are olefin sulfonates having about 12 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of α -olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO_2 , chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous SO_2 , etc., when used in the gaseous form.

The α -olefins from which the olefin sulfonates are derived are mono-olefins having 12 to 24 carbon atoms, preferably 14 to 16 carbon atoms. Preferably, they are straight chain olefins. Examples of suitable 1-olefins include 1-dodecene; 1-tetradecene; 1-hexadecene; 1-octadecene; 1-eicosene and 1-tetracosene.

In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process.

A specific anionic detergent which has also been found excellent for use in the present invention is described more fully in the U.S. Patent 3,332,880 of

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Phillip F. Pflumer and Adrian Kessler, issued July 25, 1967, titled "Detergent Composition".

Of all the above-described types of anionic surfactants, preferred compounds include sodium linear alkyl benzene sulfonate wherein the alkyl chain averages from about 10 to 18, more preferably about 12, carbon atoms in length, sodium tallow alkyl sulfate; 2-acetoxy-tridecane-1-sulfonic acid; sodium α -1-g-sulfopalmitate; sodium β -methoxy-octadecylsulfonate; sodium coconut alkyl ethylene glycol ether sulfonate; the sodium salt of the sulfuric acid ester of the reaction product of one mole of tallow alcohol and three moles of ethylene oxide; and mixtures thereof.

Ampholytic Synthetic Detergents

Ampholytic synthetic detergents can be broadly described as derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and at least one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate. Examples of compounds falling within this definition are sodium 3-(dodecylamino)-propionate, sodium 3-(dodecylamino)propane-1-sulfonate, sodium 2-(dodecylamino)ethyl sulfate, sodium 2-(dimethylamino)octadecanoate, disodium 3-(N-carboxymethyldodecylamino)-propane-1-sulfonate, disodium octadecyl-iminodiazetate, sodium 1-carboxymethyl-2-undecylimidazole, and sodium N,N-bis(2-hydroxyethyl)-2-sulfato-3-dodecoxypropylamine. Sodium 3-(dodecylamino)propane-1-sulfonate is preferred.

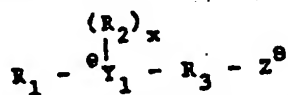
Zwitterionic Synthetic Detergents

Zwitterionic surfactants can be broadly described

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as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. The cationic atom in the quaternary compound can be part of a heterocyclic ring. In all of these compounds there is at least one aliphatic group, straight chain or branched, containing from about 3 to 18 carbon atoms and at least one aliphatic substituent containing an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphato, or phosphono. Examples of various classes of zwitterionic surfactants operable herein are described as follows:

1. Compounds corresponding to the general formula



wherein R_1 is alkyl, alkenyl or a hydroxyalkyl containing from about 8 to about 18 carbon atoms and containing if desired up to about 10 ethylene oxide moieties and/or a glyceryl moiety; Y_1 is nitrogen, phosphorus or sulfur, R_2 is alkyl or monohydroxyalkyl containing 1 to 3 carbon atoms; x is 1 when Y_1 is S, 2 when Y_1 is N or P; R_3 is alkylene or hydroxyalkylene containing from 1 to about 5 carbon atoms; and Z is a carboxy, sulfonate, sulfate, phosphate or phosphonate group. Examples of this class of zwitterionic

surfactants include 3-(N,N-dimethyl-N-hexadecylammonio)-propane-1-sulfonate; 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate; 2-(N,N-dimethyl-N-dodecylammonio)acetate; 3-(N,N-dimethyl-N-dodecylammonio)propionate; 2-(N,N-dimethyl-N-octadecylammonio)ethane-1-sulfate; 3-(P,P-dimethyl-P-dodecylphosphonio)propane-1-sulfonate; 2-(S-methyl-S-tert-hexadecylsulfonio)ethane-1-sulfonate;

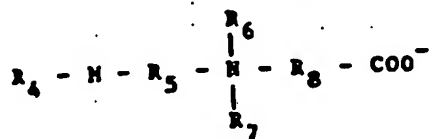
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3-(3-methyl-5-dodecylsulfonio)propionate; 4-(5-methyl-5-tetradecylsulfonio)butyrate; 3-(N,N-dimethyl-N-4-dodecylammonio)propane-1-sulfonate; 3-(N,N-dimethyl-N-2-diethoxyhexadecylammonio)propane-1-phosphate; and 3-(N,N-dimethyl-N-4-glyceryldodecylammonio)propionate.

Preferred compounds of this class from a commercial standpoint are 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate; 3-(N,N-dimethyl-N-alkylammonio)-2-hydroxypropane-1-sulfonate, the alkyl group being derived from tallow fatty alcohol; 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate; 3-(N,N-dimethyl-N-tetradecylammonio)propane-1-sulfonate; 3-(N,N-dimethyl-N-alkylammonio)-2-hydroxypropane-1-sulfonate, the alkyl group being derived from the middle cut of coconut fatty alcohol; 3-(N,N-dimethyldodecylammonio)-2-hydroxypropane-1-sulfonate; 4-(N,N-dimethyl-tetradecylammonio)butane-1-sulfonate; 4-(N,N-dimethyl-N-hexadecylammonio)butane-1-sulfonate; 4-(N,N-dimethyl-hexadecylammonio)butyrate; 6-(N,N-dimethyl-N-octadecylammonio)hexanoate; 3-(N,N-dimethyl-N-eicosylammonio)-3-methylpropane-1-sulfonate; and 6-(N,N-dimethyl-N-hexadecylammonio)hexanoate.

Means for preparing many of the surfactant compounds of this class are described in U.S. Patents 2,129,264, 2,774,786, 2,813,898, 2,828,332 and 3,529,521 and; German Patent 1,613,421.

2. Compounds having the general formula:

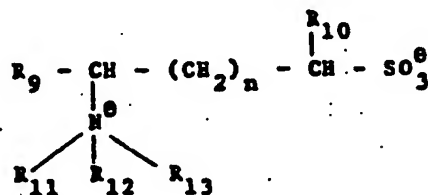


wherein R_4 is an alkyl, cycloalkyl, aryl, aralkyl or alkaryl group containing from 10 to 20 carbon atoms; N

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is a bivalent radical selected from the group consisting of aminocarbonyl, carbonylamino, carbonyloxy, amino-carbonylamino, the corresponding thio groupings and substituted amino derivatives; R_5 and R_8 are alkylene groups containing from 1 to 12 carbon atoms; R_6 is alkyl or hydroxyalkyl containing from 1 to 10 carbon atoms; R_7 is selected from the group consisting of R_6 groups R_4-M-R_5 , and $-R_8COOMe$ wherein R_4 , R_5 , R_6 and R_8 are as defined above and Me is a monovalent salt-forming cation. Compounds of the type include N,N-bis(oleylamidopropyl)-N-methyl-N-carboxymethylammonium betaine; N,N-bis(stearamidopropyl)-N-methyl-N-carboxymethylammonium betaine; N-(stearamidopropyl)-N-dimethyl-N-carboxymethylammonium betaine; N,N-bis(oleylamidopropyl)-N-(2-hydroxyethyl)-N-carboxymethylammonium betaine; and N,N-bis-(stearamidopropyl)-N-(2-hydroxyethyl)-N-carboxymethylammonium betaine. Zwitterionic surfactants of this type are preparing in accordance with methods described in U.S. Patent 3,265,719 and DAS 1,018,421.

3. Compounds having the general formula:



wherein R_9 is an alkyl group, R_{10} is a hydrogen atom or an alkyl group, the total number of carbon atoms in R_9 and R_{10} being from 8 to 16 and



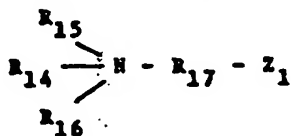
represents a

quaternary ammonio group in which each group R_{11} , R_{12}

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and R_{13} is an alkyl or hydroxyalkyl group or the groups R_{11} , R_{12} and R_{13} are conjoined in a heterocyclic ring and n is 1 or 2. Examples of suitable zwitterionic surfactants of this type include the γ and δ hexadecyl pyridino sulphobetaines, the γ and δ hexadecyl γ -picolino sulphobetaines, the γ and δ tetradecyl pyridino sulphobetaines and the hexadecyl trimethylammonio sulphobetaines. Preparation of such zwitterionic surfactants is described in South African patent application 69/5788, published 10 March 31, 1971.

4. Compounds having the general formula



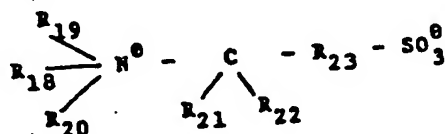
wherein R_{14} is an alkarylbenzyl group containing from about 8 to 24 carbon atoms in the alkyl chain; R_{15} is selected from the group consisting of R_{14} groups and alkyl and hydroxyalkyl groups containing from 1 to 7 carbon atoms; R_{16} is alkyl or hydroxyalkyl containing from 1 to 7 carbon atoms; R_{17} is alkylene or hydroxyalkylene containing from 1 to 7 carbon atoms and Z_1 is selected from the group consisting of sulfonate, carboxy and sulfate. Examples of zwitterionic surfactants of this type include 3-(N-dodecylbenzyl-N,N-dimethylammonio)propane-1-sulfonate; 4-(N-dodecylbenzyl-N,N-dimethylammonio)butane-1-sulfonate; 3-(N-hexadecylbenzyl-N,N-dimethylammonio)propane-1-sulfonate; 3-(N-dodecylbenzyl-N,N-dimethylammonio)propionate; 4-(N-hexadecylbenzyl-N,N-dimethylammonio)butyrate; 3-(N-tetradecylbenzyl-N,N-dimethylammonio)propane-1-sulfate; 3-(N-dodecylbenzyl-N,N-dimethylammonio)-2-hydroxypropane-

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1-sulfonate; 3-[N,N-di(dodecylbenzyl)-N-methylammonio] propane-1-sulfonate; 4-[N,N-di(hexadecylbenzyl)-N-methylammonio] butyrate; and 3-[N,N-di(tetradecylbenzyl)-N-methylammonio]-2-hydroxypropane-1-sulfonate.

Zwitterionic surfactants of this type as well as methods for their preparation are described in U.S. Patents 2,697,116; 2,697,656 and 2,669,991 and Canadian Patent 880,364.

5. Compounds having the general formula:



wherein R_{18} is an alkylphenyl, cycloalkylphenyl or alkenylphenyl group containing from 8 to 20 carbon atoms, in the alkyl, cycloalkyl or alkenyl moiety; R_{19} and R_{20} are each aliphatic groups containing from 1 to 5 carbon atoms; R_{21} and R_{22} are each hydrogen atoms, hydroxyl groups or aliphatic groups containing from 1 to 3 carbon atoms and R_{23} is an alkylene group containing from 2 to 4 carbon atoms.

Examples of zwitterionic surfactants of this type include 3-(N-dodecylphenyl-N,N-dimethylammonio)propane-1-sulfonate; 4-(N-hexadecylphenyl-N,N-dimethyl)butane-1-sulfonate; 3-(N-tetradecylphenyl-N,N-dimethylammonio)-3,3-dimethylpropane-1-sulfonate and 3-(N-dodecylphenyl-N,N-dimethylammonio)-3-hydroxypropane-1-sulfonate. Compounds of this type are described more fully in British Patents 970,883 and 1,046,252.

Of all the above-described types of zwitterionic surfactants, preferred compounds include 3(N,N-dimethyl-N-alkylammonio)-propane-1-sulfonate and 3(N,N-dimethyl-N-

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alkylammonio)-2-hydroxypropane-1-sulfonate wherein in both compounds the alkyl group averages 14.8 carbon atoms in length; 3-(N,N-dimethyl-N-hexadecylammonio)-propane-1-sulfonate; 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate; 3-(N-dodecylbenzyl-N,N-dimethylammonio)-propane-1-sulfonate; (N-dodecylbenzyl-N,N-dimethylammonio)acetate; 3-(N-dodecylbenzyl-N,N-dimethylammonio)propionate; 6-(N-dodecylbenzyl-N,N-dimethylammonio)hexanoate; and (N,N-dimethyl-N-hexadecylammonio)acetate.

Builder Salts

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The detergent compositions of the instant invention contain, as an essential component, an alkaline, polyanionic detergent builder salt. In the present compositions these water-soluble alkaline builder salts serve to maintain the pH of the laundry solution in the range of from about 7 to about 12, preferably from about 8 to about 11. Furthermore, these builder salts enhance the fabric cleaning performance of the overall compositions while at the same time serve to suspend particulate soil released from the surface of the fabrics and prevent its redeposition on the fabric surfaces. Surprisingly, although the detergency builder salts serve to suspend clay soils of the caolinite and illite types and prevent their redeposition on fabrics, they do not appear to interfere with the deposition on fabric surfaces of the smectite-type clay softeners used herein. Furthermore, these polyanionic builder salts have been found to cause the smectite-type clays present in the granular detergent formulations of the invention to be readily and homogeneously dispersed throughout the aqueous laundering medium with a minimum of agitation. The homogeneity of the clay dispersion is necessary for the clay to function effectively as a fabric

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softener, while the ready dispersability allows granular detergent compositions to be formulated.

Suitable detergent builder salts useful herein can be of the poly-valent inorganic and poly-valent organic types, or mixtures thereof. Non-limiting examples of suitable water-soluble, inorganic alkaline detergent builder salts include the alkali metal carbonates, borates, phosphates, polyphosphates, tripolyphosphates, bicarbonates, and sulfates. Specific examples of such salts include the sodium and potassium tetra-
10 borates, perborates, bicarbonates, carbonates, tripolyphosphates, orthophosphates and hexametaphosphates.

Examples of suitable organic alkaline detergency builder salts are: (1) water-soluble amino polyacetates, e.g., sodium and potassium ethylenediaminetetraacetates, nitrilotriacetates and N-(2-hydroxyethyl)nitrilodiacetates; (2) water-soluble salts of phytic acid, e.g., sodium and potassium phytates; (3) water-soluble polyphosphonates, including, sodium, potassium and lithium salts of ethane-1-hydroxy-1,1-diphosphonic acid; sodium, potassium and lithium
20 salts of methylenediphosphonic acid and the like.

Additional organic builder salts useful herein include the polycarboxylate materials described in U.S. Patent 2,264,103, including the water-soluble alkali metal salts of mellitic acid. The water-soluble salts of polycarboxylate polymers and copolymers such as are described in U.S. Patent 3,306,067, are also suitable herein. It is to be understood that while the alkali metal salts of the foregoing inorganic and organic poly-valent anionic builder salts are preferred for use herein from an economic standpoint, the ammonium,
30 alkanolammonium, e.g., triethanolammonium, diethanolammonium, and the like, water-soluble salts of any of the foregoing

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builder anions are useful herein.

Mixtures of organic and/or inorganic builders can be used herein. One such mixture of builders is disclosed in Canadian Patent 755,038, e.g., a ternary mixture of sodium tripolyphosphate, trisodium nitrilotriacetate and trisodium ethane-1-hydroxy-1,1-diphosphonate.

10 While any of the foregoing alkaline poly-anionic builder materials are useful herein, sodium tripolyphosphate, sodium nitrilotriacetate, sodium mellitate, sodium citrate and sodium carbonate are preferred herein for this builder use. Sodium tripolyphosphate is especially preferred herein as a builder both by virtue of its detergency builder activity and its ability to homogeneously and quickly disperse the smectite clays throughout the aqueous laundry media without interfering with clay deposition on the fabric surface. Sodium tripolyphosphate is also especially effective for suspending illite and kaolinite clay soils and retarding their redeposition on the fabric surface.

20 The detergent builders are used at concentrations of from about 10% to about 60%, preferably 20% to 50%, by weight of the detergent compositions of this invention.

Clay Compounds

The third essential component of the present compositions consists of particular smectite clay materials to provide fabric softening concurrently with fabric cleansing. These smectite clays are present in the detergent compositions at levels from about 1% to about 50%, preferably from 5% to 15% by weight, of the total compositions.

30 The clay minerals used to provide the softening properties of the instant compositions can be described as expandable, three-layer clays, i.e., alumino-silicates and

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magnesium silicates, having an ion exchange capacity of at least 50 meq/100 g. of clay. The term "expandable" as used to describe clays relates to the ability of the layered clay structure to be swollen, or expanded, on contact with water. The three-layer expandable clays used herein are those materials classified geologically as smectites.

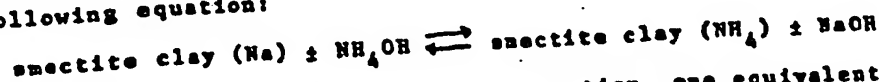
10 There are two distinct classes of smectite-type clays; in the first, aluminum oxide is present in the silicate crystal lattice; in the second class of smectites, magnesium oxide is present in the silicate crystal lattice. The general formulas of these smectites are $Al_2(Si_2O_5)_2(OH)_2$ and $Mg_3(Si_2O_5)_2(OH)_2$, for the aluminum and magnesium oxide type clay, respectively. It is to be recognized that the range of the water of hydration in the above formulas can vary with the processing to which the clay has been subjected. This is immaterial to the use of the smectite clays in the present invention in that the expandable characteristics of the hydrated clays are dictated by the silicate lattice structure. Furthermore, atom substitution by iron and magne-
20 sium can occur within the crystal lattice of the smectites, while metal cations such as Mn^{++} , Ca^{++} , as well as H^+ , can be co-present in the water of hydration to provide electrical neutrality. Except as noted hereinafter, such cation substitutions are immaterial to the use of the clays herein since the desirable physical properties of the clays are not substantially altered thereby.

30 The three-layer, expandable aluminosilicates useful herein are further characterized by a dioctahedral crystal lattice, while the expandable three-layer magnesium silicates have a trioctahedral crystal lattice.

As noted hereinabove, the clays employed in the

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compositions of the instant invention contain cationic counterions such as protons, sodium ions, potassium ions, calcium ion, magnesium ion, and the like. It is customary to distinguish between clays on the basis of one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is predominantly sodium. Such absorbed cations can become involved in exchange reactions with cations present in aqueous solutions. A typical exchange reaction involving a smectite-type clay is expressed by the following equation:



Since in the foregoing equilibrium reaction, one equivalent weight of ammonium ion replaces an equivalent weight of sodium, it is customary to measure cation exchange capacity (sometimes termed "base exchange capacity") in terms of milliequivalents per 100 g. of clay (meg./100 g.). The cation exchange capacity of clays can be measured in several ways, including by electro-dialysis, by exchange with ammonium ion followed by titration or by a methylene blue procedure, all as fully set forth in Grimshaw, "The Chemistry and Physics of Clays", pp. 264-265, Interscience (1971). The cation exchange capacity of a clay mineral relates to such factors as the expandable properties of the clay, the charge of the clay, which, in turn, is determined at least in part by the lattice structure, and the like. The ion exchange capacity of clays varies widely in the range from about 2 meg/100 g. for kaolinites to about 150 meg/100 g., and greater, for certain clays of the montmorillonite variety. Illite clays have an ion exchange capacity somewhere in the lower portion of the range, i.e., around 26 meg/100 g. for an average illite clay.

It has been determined that illite and kaolinite

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clays, with their relatively low ion exchange capacities, are not useful in the instant compositions. Indeed, such illite and kaolinite clays constitute a major component of clay soils and, as noted above, are removed from fabric surfaces by means of the instant compositions. However, smectites, such as nontronite, having an ion exchange capacity of approximately 50 meg/100 g., saponite, which has an ion exchange capacity of around 70 meg/100 g., and montmorillonite, which has an ion exchange capacity greater than 70 meg/100 g., have been found to be useful in the instant compositions in that they are deposited on the fabrics to provide the desired softening benefits. Accordingly, clay minerals useful herein can be characterized as expandable, three-layer smectite-type clays having an ion exchange capacity of at least about 50 meg/100 g.

While not intending to be limited by theory, it appears that the advantageous softening (and potentially dye scavenging, etc.) benefits of the instant compositions are ascribable to the physical characteristics and ion exchange properties of the clays used therein. That is to say, experiments have shown that non-expandable clays such as the kaolinites and the illites, which are both classes of clays having ion exchange capacities below 50 meg/100 g., do not provide the beneficial aspects of the clays employed in the instant compositions. Furthermore, the unique physical and electrochemical properties of the smectite clays apparently cause their interaction with, and dispersion by, the poly-anionic builder salts used in the instant compositions. Thus, it has now been found that, rather than agglomerating to form viscous gels when contacted by water, the smectite clays used herein can be added to aqueous laundry baths in granular compositions containing poly-anionic detergency builders of

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the type disclosed herein to yield homogeneous, stable clay suspensions. The problems of settling and agglomeration usually encountered when smectite clays are added to aqueous media in solid form are alleviated by the presence of the builder. Apparently, the negative electrical charges on the builder anions serve to repulse the clay particles, thereby providing the desired homogeneous clay dispersion and preventing agglomeration. Whatever the reason for the advantageous co-action of the detergency builder and smectite clays used herein, the combination of the poly-anionic detergency builders with the expandable, three-layer, dioctahedral aluminosilicates and expandable, three-layer, trioctahedral magnesium silicates provides a means whereby such smectite clays can be added to a surfactant-containing media in solid form to provide the homogeneous clay dispersion required for effective fabric softening.

The smectite clays used in the compositions herein are all commercially available. Such clays include, for example, montmorillonite, volchonskoite, nontronite, hectorite, saponite and sauconite. The clays herein are available under various trademarks, for example, Thixogel #1* and Gelwhite GP* from Georgia Kaolin Co., Elizabeth, New Jersey; Volclay BC* and Volclay #325*, from American Colloid Co., Skokie, Illinois; Black Hills Bentonite BH450*, from International Minerals and Chemicals; and Veegum Pro* and Veegum V*, from R.T. Vanderbilt. It is to be recognized that such smectite-type minerals obtained under the foregoing trademarks can comprise mixtures of the various discreet mineral entities. Such mixtures of the smectite minerals are suitable for use herein.

While any of the smectite-type clays having a cation

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exchange capacity of at least about 50 meq/100 g. are useful herein, certain clays are preferred. For example, Gelwhite GP is an extremely white form of smectite clay and is therefore preferred when formulating white granular detergent compositions. Volclay BC, which is a smectite-type clay mineral containing at least 3% of iron (expressed as Fe_2O_3) in the crystal lattice, and which has a very high ion exchange capacity, is one of the most efficient and effective clays for use in laundry compositions and is preferred from the standpoint of product performance. On the other hand, certain smectite clays marketed under the name "bentonite" are sufficiently contaminated by other silicate minerals that their ion exchange capacity falls below the requisite range, and such clays are of no use in the instant compositions.

Appropriate clay minerals for use herein can be selected by virtue of the fact that smectites exhibit a true 14\AA x-ray diffraction pattern. This characteristic pattern, taken in combination with exchange capacity measurements performed in the manner noted above, provides a basis for selecting particular smectite-type minerals for use in the granular detergent compositions disclosed herein.

Optional Components

The detergent compositions disclosed herein can contain other materials commonly used in such compositions. For example, various soil-suspending agents such as carboxymethylcellulose, corrosion inhibitors, dyes, fillers such as sodium sulfate and silica, optical brighteners, suds boosters, suds depressants, germicides, anti-tarnishing agents, pH adjusting agents such as sodium silicate, enzymes, and the like, well-known in the art for use in detergent compositions, can also be employed herein. Bound water can also be present

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in said detergent compositions.

The clay-containing detergent compositions of this invention are in granular form. The compositions can be prepared by simply admixing the appropriate ingredients in dry form. The compositions are then added to water to provide a laundering liquor containing the instant compositions to the extent of from about 0.02% to about 2% by weight.

10 Soiled fabrics are added to the laundering liquor and cleaned in the usual manner. The effective amount of the detergent compositions to be used will depend to an extent on the weight of clothes being laundered and their degree of soiling. Aqueous laundering baths containing said compositions provide adequate cleaning and softening benefits with soiled fabrics, especially cotton and cotton/polyester blends. The suspended clay material found in the laundering liquor also serves to adsorb fugitive dye in solution, thereby reducing or inhibiting dye transfer.

20 The granular built detergent compositions and the fabric laundering and softening process of the instant invention are illustrated by the following examples. Desized cotton terry washcloths were washed in aqueous solutions having dissolved therein various clay-containing built granular detergent compositions of the instant invention. Softness of the terry swatches so washed was compared with the softness of terry swatches washed in an equivalent concentration of the same built granular detergent without the clay, as well as with the softness of terry swatches washed in this same no-clay detergent solution followed by rinsing in water containing a commercially available fabric softener, Downy. Composition and solution

30 concentrations are described in Table I below.

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The terry swatches were washed for 10 minutes in a miniature agitator containing two gallons of washing liquor at 120°F. and 7 gr/gal. artificial hardness. The swatches comprised 4% by weight of the washing liquor. After washing, the swatches were spun dry and rinsed with two gallons of water at 120°F. and 7 grains/gallon artificial hardness. Swatches were then dried in a conventional electric dryer.

After several treatment cycles, the test and control swatches were graded tactilely for softness by a panel of three to five judges making paired comparisons of all swatches. Graders assigned an integer grade of from 0 to 4 on a linear scale to the softer treatment of each pair, assigning the higher grades to corresponding larger differences in softness.

The data obtained were analyzed statistically to obtain mean softness grades (panel score units) for each treatment and a statistical estimate of the least significant difference (LSD) at the 95% confidence level. Results of the softening tests appear in Table I.

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TABLE 1

Component - Wt. %	Composition No.					
	1	2	3	4	5	6
Anionic Surfactant*	16.8	16.8	16.8	15.3	8.4	16.8
Sodium tripolyphosphate	32.9	32.9	32.9	45.0	24.7	49.5
Sodium Silicate	5.9	5.9	5.9	5.37	2.9	5.9
5 Sodium Sulfate	19.6	29.6	29.6	12.8	7.0	14.1
Miscellaneous minors	4.1	4.1	4.1	2.8	1.6	3.1
Gelwhite GP**	10.0					
Volclay BC***				9.1	50.0	
Moisture	← Balance →					
10 Solution Concentration (Wt. % of Composition)	0.104	0.104	0.104	0.11	0.20	0.104
Solution pH	9.5	9.2	9.2	9.3	9.3	9.2
Rinse	Water	Water	Downy (0.07 wt.)	Water	Water	Water
Number of Cycles	4	4	4	2	2	2
Mean Softness Grade (Panel Score Units)	0.8	-2.1	0.2	-0.5	1.7	-2.6
15 Least Significant Difference (LSD)	0.9			1.0		

* A mixture in a 1.22:1 wt. ratio of sodium tallow alkyl sulfate and sodium linear alkyl benzene sulfonate wherein the alkyl chain of the sulfonate averages 11.8 carbon atoms in length.

20 ** A commercially-available sodium montmorillonite clay having an ion-exchange capacity of about 100 meq./100 g.

*** A commercially-available sodium montmorillonite clay having an ion-exchange capacity of about 85-100 meq./100 g.

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It can be seen from Table I that Compositions 1, 4 and 5 of the instant invention provide softening benefits superior to built detergent formulations containing no clay softening agents and softening benefits comparable to those obtained with a commercial fabric softening rinse additive.

Compositions 1, 4 and 5 of the instant invention also provide excellent cleaning and detergency when employed in washing solutions at the specified concentrations.

Substantially similar detergency and softening results are obtained when the anionic surfactant mixture in Composition 1, 4 or 5 (Table I) is replaced with an equivalent amount of 2-acetoxy-tridecane-1-sulfonic acid; sodium methyl- α -sulfopalmitate; sodium β -methoxyoctadecyl-sulfonate; sodium coconut alkyl ethylene glycol ether sulfonate or the sodium salt of the sulfuric acid ester of the reaction product of one mole of tallow fatty alcohol and three moles of ethylene oxide.

Substantially similar detergency and softening are obtained when the anionic surfactant mixture in Composition 1, 4 or 5 (Table I) is replaced with an equivalent amount of 3(N,N-dimethyl-N-alkylammonio)-propane-1-sulfonate or 3(N,N-dimethyl-N-alkylammonio)-2-hydroxypropane-1-sulfonate wherein in both compounds the alkyl group averages 14.8 carbon atoms in length; 3(N,N-dimethyl-N-hexadecylammonio)-propane-1-sulfonate; 3(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate; 3-(N-dodecylbenzyl-N,N-dimethylammonio)-propane-1-sulfonate; (N-dodecylbenzyl-N,N-dimethylammonio)acetate; 3-(N-dodecylbenzyl-N,N-dimethylammonio)propionate; 6-(N-dodecylbenzyl-N,N-dimethylammonio)hexanoate; (N,N-dimethyl-N-hexadecylammonio)-acetate, or sodium 3-(dode-

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Substantially similar detergency and softening are obtained when the sodium tripolyphosphate builder in Composition 1, 4 or 5 (Table I) is replaced with an equivalent amount of sodium nitrilotriacetate, sodium mellitate, sodium citrate or sodium carbonate.

Substantially similar detergency and softening are obtained when the clay softening agent in Compositions 1, 4 or 5 (Table I) is replaced with an equivalent amount of volchonskoite, nontronite, hectrite or sauconite all such clays having an ion-exchange capacity greater than 50
10 meq./100 g.

In addition to the unexpected fabric softening benefits which the built laundry detergent compositions of this invention provide, there are other advantages which this invention makes possible. For instance, dye-transfer inhibition noted above is a significant advantage not commonly shared by ordinary fabric softening compositions.

Moreover, the particular class of clays described herein which are deposited on the fabrics provide a soil-
20 release benefit. The clays are adsorbed by the fabrics being washed providing an improved soil-release surface. The benefit from this treatment is that during subsequent washings, stains and soils are more easily removed from the fabrics as compared to a fabric which has not previously been exposed to a treatment by the clay-containing compositions of this invention. Still further, all of these benefits are enjoyed without impairing the water-absorbent qualities of the treated fabric. This is in marked contrast with ordinary quaternary ammonium fabric softeners which may tend to

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It is especially significant that each of the advantages described above in no way impair or interfere with the general overall cleaning effectiveness of the detergent composition. The fact that these achievements are attained during the relatively brief span of a short washing cycle, for example about 6 to about 15 minutes, is especially noteworthy.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A granular, built laundry detergent composition
comprising:

- (a) from about 2% to about 30% by weight of a
non-soap synthetic detergent compound selected
from the group consisting of anionic synthetic
detergents,
ampholytic synthetic detergents, zwitterionic
synthetic detergents and mixtures thereof;
- (b) from about 10% to about 60% by weight of an
organic or inorganic detergent builder salt; and
- (c) from about 1% to about 50% by weight of a
smectite-type clay softening agent having an ion
exchange capacity of at least about 50 meq/100 g.,

said composition providing a solution pH of from about 7
to about 12 when dissolved in water at a concentration of
about 0.12% by weight.

2. A composition in accordance with Claim 1

- (a) wherein the synthetic detergent compound is an
anionic synthetic detergent and is present to the
extent of from about 5% to about 20% by weight;
- (b) wherein the builder salt is selected from the
group consisting of alkali metal carbonates,
alkali metal borates, alkali metal phosphates,
alkali metal polyphosphates, alkali metal
tripolyphosphates, alkali metal bicarbonates,
alkali metal sulfates, water-soluble amino
polyacetates, water-soluble salts of phytic
acid, and water-soluble polyphosphonates and
is present to the extent of from about 20% to

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about 50% by weight; and

(c) wherein the smectite-type clay softening agent is selected from the group consisting of dioctahedral expandable three-layer aluminosilicates and trioctahedral expandable three-layer magnesium silicates and is present to the extent of from about 5% by weight to about 15% by weight.

3. A composition in accordance with Claim 2 wherein the smectite clay softening agent is selected from the group consisting of montmorillonites, volchonkoites, nontronites, hectorites and saucroites.

4. A composition in accordance with Claim 3 wherein the anionic surfactant is a water-soluble salt of an organic sulfuric reaction product containing an alkyl group of from about 8 to about 22 carbon atoms and a moiety selected from the group consisting of sulfuric acid ester moieties and sulfuric acid ester moieties.

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5. A composition in accordance with Claim 4 wherein the anionic surfactant is selected from the group consisting of sodium linear alkyl benzene sulfonate wherein the alkyl chain averages from about 10 to 18 carbon atoms in length, sodium tallow alkyl sulfate; 2-acetoxy-tridecane-1-sulfonic acid; sodium methyl-g-sulfopalmitate; sodium 8-methoxyoctadecylsulfonate; sodium coconut alkyl ethylene glycol ether sulfonate; the sodium salt of the sulfuric acid ester of the reaction product of one mole of tallow fatty alcohol and three moles of ethylene oxide; and mixtures thereof.

6. A composition in accordance with Claim 5 wherein the builder salt is selected from the group consisting of sodium tripolyphosphate, sodium nitrilotriacetate, sodium mellitate, sodium citrate and sodium carbonate.

7. A composition in accordance with Claim 6 wherein the smectite-type clay softening agent is montmorillonite.

8. A composition in accordance with Claim 7 wherein the smectite-type clay softening agent is a sodium montmorillonite clay having an ion-exchange capacity of about 100 meq/100 g.

9. A composition in accordance with Claim 7 wherein the smectite-type clay softening agent is a sodium montmorillonite clay having an ion-exchange capacity of 85-100 meq/100 g.

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10. A granular, built laundry detergent composition comprising:

- (a) from about 5% to about 20% of a mixture, in a 1.22:1 weight ratio, of sodium tallow alkyl sulfate and sodium linear alkyl benzene sulfonate wherein the alkyl chain of the sulfonate averages about 12 carbon atoms in length;
- (b) from about 20% to about 50% of a sodium tripolyphosphate builder salt; and
- (c) from about 5% to about 15% of a sodium montmorillonite clay softening agent having an ion-exchange capacity of about 100 meq/100 g.

11. A process for the simultaneous laundering and softening of fabrics comprising contacting said fabrics with an aqueous medium containing from about 0.02% by weight to about 2% by weight of a composition in accordance with Claim 1.